
A Radial Probability Density Function for Analysis of Canonical Molecular Orbitals

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ABSTRACT: A one-dimensional probability density function, analogous to the atomic radial density for the hydrogen atom, $r^2 R_{nl}(r)$, is defined for an arbitrary three-dimensional density. It is obtained numerically by taking the derivative of a cumulative probability distribution with respect to the cubic root of the volume enclosed by each in a series of isosurfaces. Each point in the function is associated with a unique isosurface, and the isosurface associated with the maximum of the defined function represents the most probable isosurface with respect to the putative radius. This function therefore provides an objective selection criterion for a single isosurface to represent a three-dimensional density. This technique is applied to set of canonical molecular orbitals. The selected threshold value varies from orbital to orbital, but the enclosed probability falls in the range of 20% to 55% for the reported orbitals. In all cases, the enclosed probability is much smaller than the common choices found in the literature. The concomitant smaller volume often makes possible a more localized interpretation and helps to clarify the conventional delocalized interpretation of molecular orbitals. For example, the isosurface plots selected by this method distinguish the formally bonding orbital in He_2 from the true bonding orbital in H_2 . Examples from N_2 , F_2 , HF , H_2O , C_2H_6 , and $\text{Ni}(\text{CO})_4$ are also presented. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 310–321, 2000

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Introduction

Rigorously calculated, graphical representations of canonical molecular orbitals have been used in the interpretation of quantum calculations at all levels of quality for decades.^{1–10} Such

representations, however, have suffered from ambiguities in chemical interpretation. To overcome this problem, orbital localization schemes¹¹ and rigorous techniques for the graphical interpretation of the total density¹² have achieved some notable success. These methods as well as valence bond techniques, however, sacrifice the orbitals' energy ordering and the phase information that have proved qualitative molecular orbital theory so useful for a wide range of chemical problems.^{13–18}

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As Dunning and Winter pointed out,³ the plotting of molecular orbitals is a problem in four dimensions and requires one of the variables “be assigned a somewhat arbitrary value.” In the orbital plots presented in the current study, a single value of the wave function is chosen to create a molecular surface in three dimensions.¹⁹ All points in space where the wave function has a given value, or the negative of that value, are depicted as a three-dimensional surface. All other points in space are ignored—both internal and external to the surface. By analogy to geographical maps, this single value of the wave function is sometimes referred to as a contour level, and the plot itself is referred to as a contour map. For three-dimensional depictions, the selected value of the wave function is sometimes called the threshold, and the contour map, an isosurface. By whatever name, these plots are analogous to viewing a mountain as a two-dimensional, closed curve in which the mountain is, say, precisely 1000 meters above sea level. As the contour level gets lower (closer to sea level), the size of the curve will usually grow larger; as it gets higher (closer to the peak), the size grows smaller. Because the shape of the mountain changes as the elevation changes, a single contour level cannot provide an adequate description of a mountain or, more pertinently, a molecular orbital. In fact, any contour map of an orbital, whether two- or three-dimensional, only represents some small subset of the total information in the orbital. Some technique is needed to summarize the information contained in the four-dimensional functions that describe molecular orbitals.

One way to address this problem is to view several different contour maps simultaneously. The Density Domain Approach to chemical bonding uses this method for analyzing the total electron density in three dimensions.¹⁹ For canonical molecular orbitals, two-dimensional plots with several thresholds on one graph are a common approach. For many molecules, two-dimensional plots can be troublesome because the complexity of the spatial distribution requires more than one plane to be depicted. Interpreting a single contour plot in three dimensions for each orbital would be a helpful simplification because of the possibility of a large number of orbitals for a single molecule. A simple example is sufficient to show the inherent difficulties in such interpretations, however.

Figure 1 shows the $2A_1$ valence orbital of hydrogen fluoride at various contour levels. The plotted surfaces can thus be viewed as a function of contour level where we go from a tiny surface to a large surface as the contour level goes from its highest value

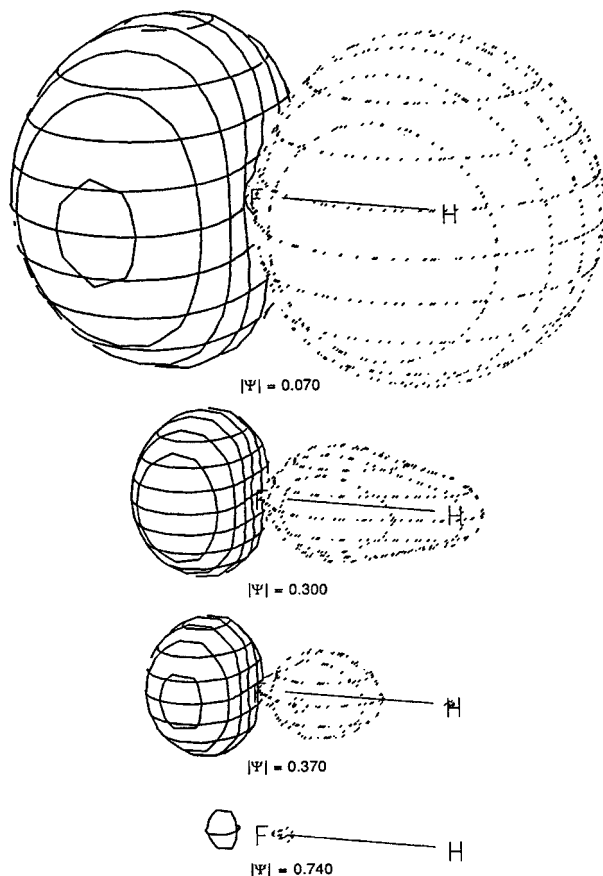


FIGURE 1. The $2A_1$ valence orbital of HF shown at various contour levels.

toward zero. Note the change in shape of the orbital as the contour level changes. This change in topological type is sometimes called a bifurcation and is a common feature of molecular orbitals for molecules of even small size. Obviously, the perception of the chemical role would depend strongly on which contour level (or threshold) is chosen. The higher contour levels, 0.370 and 0.740, might be interpreted as a fluorine lone pair because of both the absence of a contribution from the hydrogen atom and the imbalance in distribution on the two sides of the fluorine atom. On the other hand, the lower contour levels, 0.300 and 0.070, include some F—H bonding character, as indicated by the constructive interference between the two atoms. The use of several contour maps allows for several interpretations but does not provide a criterion for assessing their relative importance.

Dunning and Winter³ suggested that the appropriate contour level was where the shape of the orbital quit changing as the contour level increased. This criterion yielded orbital plots that are more lo-

calized than the now customary, low contour plots, but only a small number of orbitals were so plotted. As there can be several such changes in shape for a molecular orbital, a choice between apparently equal representations still arises. A criterion based on quantitative arguments is preferable.

The customary choice of contour level for molecular orbital isosurface plots has been low, corresponding to a large, enclosed probability usually in a range from 70% to 90%.^{5,8} Gerhold et al.²⁰ proposed a criterion of 90% so that the plots of atomic orbitals would extend out to the van der Waals radii. When interpreting the role of an orbital in the chemical bonding within a compound, a criterion of the smaller, covalent radii appears more appropriate. Furthermore, enclosed probability can be an inherently deceptive criterion because the chance of finding the electron at any point near the displayed surface is quite small. The electron would on average be found at some point deep inside the drawn surface. A median value is generally considered appropriate for describing the average in a skewed distribution and, without knowledge of the probability distribution, would appear to be the best choice for molecular orbital isosurfaces. Fortunately, as shown in what follows, a radial probability distribution can be determined for an arbitrary molecular orbital.

The familiar probability density function of the hydrogen atom,²¹ which is the derivative of the probability with respect to radius, is an example of a radial probability distribution that could be used to evaluate the chance of finding an electron at or near the plotted surface. To determine a similar distribution for a molecular orbital, a putative radius must be defined. The cubic root of the volume enclosed by each contour level (threshold value) is used as the definition in this work. Thus, the function to be defined is a derivative of total enclosed probability with respect to a putative radius—the cubic root of the enclosed volume. The examples show how this distribution can be used to assess the relative importance of different isosurfaces for a three-dimensional density. Each point in the function is associated with a unique isosurface, and the maximum of the defined function represents the most probable isosurface with respect to the putative radius. This function allows for the determination of an appropriate isosurface without artificial constraints so that the wave function itself can be said to determine the appropriate isosurface. This technique, applicable to any three-dimensional density, has been applied to occupied, canonical molecular orbitals, because, although the angular

(phase) contributions have been studied in enormous detail, the radial contributions have scarcely been considered. The study of unoccupied orbitals is not reported here because little additional information came from use of the proposed function on examples of these types of orbitals. As shown in what follows, this one-dimensional function can be readily interpreted and provides the missing information needed to evaluate quantitatively isosurface plots of molecular orbitals.

Computational Method

For a given molecular orbital, $\Psi(x, y, z)$, and a given contour level, κ , where $\kappa = |\Psi(x_1, y_1, z_1)|$ at some point x_1, y_1, z_1 , we obtain the probability of the electron residing within the surface enclosed by $|\Psi(x, y, z)| = \kappa$ by numerical integration. To this end, the chosen space surrounding the atoms in the molecule is divided into small segments of approximately 0.05 to 0.15 bohr (depending on the desired smoothness of the curve) with i such units in the x direction, j units in the y direction, and k units in the z direction. For main group elements, the limits of the space around the molecule was chosen to be in the range of 2 to 3 bohr beyond the extremes of the nuclear positions within the molecule. The precise distance was determined by the close approach of the contained probability to unity by a trial-and-error process. Usually less than 1/10,000 of the probability is outside of the chosen space for the final calculations. The probability of finding an electron inside the surface enclosed by $|\Psi(x, y, z)| = \kappa$ is:

$$\text{Prob}(\kappa) = \sum_i \sum_j \sum_k \Psi^2(i\Delta x, j\Delta y, k\Delta z) \Delta x \Delta y \Delta z$$

for all $|\Psi(i\Delta x, j\Delta y, k\Delta z)| \geq \kappa$. Δx , Δy , and Δz are the fixed, arbitrary divisions used in the x , y , and z directions.

For each κ , there is a unique surface defined by the set of all points in space where $|\Psi(x, y, z)| = \kappa$. It encloses a volume $V(\kappa)$. Because of this one-to-one correspondence between contour level and volume, the probability can be viewed as a function of volume. We, therefore, define a new function:

$$f(\kappa) = d\text{Prob}/dV^{1/3}(\kappa) \\ = (\text{Prob}(\kappa_1) - \text{Prob}(\kappa_2)) / (V^{1/3}(\kappa_1) - V^{1/3}(\kappa_2))$$

which holds true for numerical integration for a sufficiently small change between κ_1 and κ_2 . In practice, a difference of 0.005 is sufficient with the more critical parameters for a smooth curve being the sizes

of Δx , Δy , and Δz . It is asserted that this function determines a one-dimensional probability density function for each orbital and that this function depends on the effective radial distance, $V^{1/3}$, from the density maximum. For convenience, and to avoid confusion, this new function, $f(\kappa)$, is called ProDen (probability density).

Molecular orbital calculations on compounds exclusively composed of main group elements were performed at the Hartree–Fock level using the 6-31G*²² basis set at experimental geometries. For $\text{Ni}(\text{CO})_4$, also at its experimental geometry, the metal was described with a contracted Wachter's basis set²³ for the s and p shells with the d orbitals being that proposed by Rappe et al.²⁴; 3-21G²⁵ was used on carbon and oxygen. All calculations were performed with the GAUSSIAN-86 system of programs.²⁶ All orbital plots were produced using the plotting program of Jorgensen.²⁷ A FORTRAN program, written by the author, performed the ProDen calculations using the checkpoint file produced by the GAUSSIAN program as input. The program has since been modified to use output of GAUSSIAN's CUBE keyword. The default values for this command work well for valence orbitals of the s and p shells, but are not fine enough for core and d orbitals and are too fine for the delocalized LUMOs.

Concerning computational efficiency, the calculation of the function itself requires a small amount of time compared with that necessary for the calculation of the value of a molecular orbital at 10^6 points in space. When calculating the function for several orbitals simultaneously, the manipulation of the large CUBE data file can often add an amount of time comparable to the calculation of the grid.

Discussion of Methodology

An obvious alternative to the cubic root of the volume is the use of the contour level (amplitude) itself. However, the contour level cannot be assessed directly from the plot. That is, there is no direct visual representation of the amplitude. Even in multicontour, two-dimensional plots in which one is depicting the effects of contour variation, a key must be provided that details the value of the amplitude for each contour line. In contrast, the cubic root of the volume can be evaluated roughly from simply looking at a plot. Indeed, given a ruler and a scale, a reasonable estimate of the cubic root of the volume could be obtained in many cases. Thus, the observer would correctly sense that two isosurfaces of similar size on the same molecule would have

comparable values of the cubic root of the volume. There is simply no comparable connection between the amplitude and an orbital plot. The same amplitude for two different orbitals on the same molecule can yield isosurfaces that are quite different in size. Consider a 1s orbital in carbon versus a valence orbital. For any given amplitude, the associated isosurface for the 1s will be much smaller than that for a valence orbital, but there would be no way to determine that the two isosurfaces were associated with the same amplitude from the plot alone. Thus, the amplitude (or contour level) has an obscure physical meaning, and it is desirable to choose a variable associated with a clearer physical meaning.

Nevertheless, the maximum in the derivative of probability with respect to amplitude can be said to produce the most probable contour level with respect to contour variation. However, preliminary results show that this function has no similarity with the familiar radial probability density functions for the atomic, analytical functions. A plot of this derivative of probability versus amplitude for various molecular orbitals produced unexpected shapes that have lead to difficulty in interpretation, and a significantly greater computational effort (at least a factor of 100) was necessary to obtain a smooth curve. This combination of problems makes this alternative less useful, especially in light of the successes reported in what follows when the cubic root of the volume is used. Because of the unusual shape of the curves generated in molecules, further discussion of the utility of this alternative function is appropriate for a separate investigation and will not be pursued here.

An important feature of the ProDen function is that it starts at zero, goes through a maximum, and goes to zero as the volume goes to infinity in close imitation of the probability density functions of the hydrogen atom. The origin of the function occurs where the density of the wave function reaches a maximum. In many cases, this definition of the origin means that the origin is a set of points distributed in space. For example, a 2p orbital will have an origin that is the two points at the center of the two lobes. At an extremely low density the function goes back toward zero as a result of the exponential dependence of the radial distribution overwhelming the increase in volume—just as in the atomic probability densities. Because the ProDen function is the product of both the increasing volume and the decreasing density, there will be at least one maximum somewhere between the origin and infinity.

The case of the hydrogen 1s orbital will illustrate several important points about the ProDen function. Consider a function of the type, $\Psi = (1/\pi)^{1/2} \exp(-r)$. For $\kappa = 0.1 = \Psi(r)$, $r_\kappa = 1.730$ bohr. In this case, the isosurface associated with the contour level would be a sphere surrounding the hydrogen nucleus with a radius of 1.730 bohr. The probability of finding the electron inside this sphere (or contour level) is given by the equation:

$$\text{Prob}(\kappa) = \int_0^{r_\kappa} [(1/\pi)^{1/2} \exp(-r)]^2 r^2 dr \\ \times \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$$

For the hydrogen atom in spherical coordinates, the r associated with a given contour level is the same as the radial variable defined in the analytical solution. To obtain the analytical form of the ProDen function just proposed, we take the derivative of the function with respect to the cubic root of the volume; that is, $V^{1/3} = ((4/3)\pi)^{1/3}r$. Thus:

$$\begin{aligned} dP/d(V^{1/3}) &= (dP/dr)(dr/d(V^{1/3})) \\ &= [(1/\pi)^{1/2} \exp(-r)]^2 r^2 4\pi ((4/3)\pi)^{-1/3} \\ &= (r^2 R_{10}^2 4\pi) ((4/3)\pi)^{-1/3} \end{aligned}$$

The term $r^2 R_{10}^2$ is the well-known radial probability distribution that yields the probability per unit length that an electron will be found at a particular distance, r , from the nucleus. Thus, the new function will differ from the well-known function only by the constant 4π (the integral of θ and ϕ) and the $((4/3)\pi)^{-1/3}$ term.

Note that the maximums for both the ProDen function and $r^2 R_{10}^2$ occur at the same value of r (unity) and thus would be associated with the same isosurface. In contrast, the comparable function for the derivative with respect to contour is:

$$\begin{aligned} dP/d\kappa &= (dP/dr)/(d\kappa/dr) \\ &= -[(1/\pi)^{-1/2} \exp(-r)] r^2 4\pi \end{aligned}$$

This function has a minimum, as opposed to a maximum, that occurs at twice the radius of $r^2 R_{10}^2$ and, thus, would be associated with a significantly different threshold and isosurface.

For the hydrogen 2p orbitals, the relationship between ProDen and the usual probability density function is murkier. Take, for example, $\Psi = 1/4(1/2\pi)^{1/2}(r) \exp(-r/2) \cos \theta$. There is a range of r_κ values for a given threshold κ . A numerical solution for $\kappa = 0.05$ with $\theta = 0$ yields $r_\kappa = 0.72$ and 4.30. On the other hand, the cubic root of the volume would yield a value somewhere between

these two values. Assuming a spherical shape, and taking into account the presence of two lobes, we might estimate the cubic root of the volume as 3.64. Thus, the definition of enclosed volume for the ProDen calculation is not a simple function of the distance from the nucleus, and the connection between volume enclosed at a given threshold and r has been lost.

This difference between ProDen and the well-known radial probability density function of a 2p orbital is understood in light of the definition of the origin. The ProDen function will have two points of origin—one on each side of the nucleus at the density maxima for each lobe—as opposed to the nucleus. Multiple points of origin occur often in the ProDen calculations for molecular orbitals. Each lobe of a molecular orbital will have a density maximum at its center, and each maximum corresponds to an origin of a contribution to the volume. A molecular orbital with several lobes thus can be thought of as having just as many origins to the ProDen function. As demonstrated next, such considerations have only a small effect in the interpretation of chemical phenomena.

Results

After the ProDen calculation is complete for a given orbital, the molecular orbital itself is plotted at the contour level corresponding to the maximum of the ProDen function. In principle, this surface depicts the most probable surface with respect to the putative radius for the electrons in this orbital. In the case of a single, well-defined maximum, the three-dimensional orbital plot may be used directly to identify the orbital as either a bond pair or lone pair according to the location of the isosurface within the framework of the molecule. A broad peak is indicative of a delocalized orbital that may be composed of the same feature spread over several atoms. An example would be the π bonding in a benzene ring. In the case of low symmetry molecules, a broad peak may be associated with several different features of similar energy (a lone pair in one part, a bond pair in another portion of the molecule). In the case of an orbital with several local maxima, different features are distinguished in the same orbital. These salient features are interpreted by examining the orbital plots at each of the associated contour levels and can be evaluated quantitatively by either the value of the ProDen function or the contained probability.²⁸ Under many circumstances an isosurface plot of the outer maximum would suf-

fice because the nature of the inner peak may be deduced from the one plot.

Typically, the surfaces associated with the maximum are small and contain only about 40% of the electron probability. Therefore, they present a relatively localized picture compared with plots from the literature. Several specific examples follow to illustrate this technique.

He₂ and H₂. In the qualitative molecular orbital description of either a hydrogen or helium dimer, one orbital is described as a bonding orbital, whereas the higher energy orbital is described as antibonding. The bonding orbital of He₂ would essentially look the same as the bonding orbital in H₂. Although this observation is very misleading and obviously should not be seen in a high-quality calculation, the choice of a very low contour level could lead to similar orbital plots for the two species and precisely this erroneous conclusion.

Figure 2 presents plots of the ProDen functions for both the H₂ and He₂ bonding orbitals along with a plot of each orbital at the contour levels (thresholds) associated with the maxima in these functions. The three-dimensional plot of the H₂ orbital encloses only 34% of the electron density, but shows

sufficient electron density between the nuclei for a convincing σ bond (hereafter, 34% enclosed probability will be referred to as 34% ep). In the case of He₂, there is no obvious build-up of electron density between the nuclei (28% ep). Thus, although symmetry and simple molecular orbital theory suggests that the lowest energy He₂ orbital is the same as the only occupied orbital in H₂, the maximum in the ProDen function is associated with a contour plot easily designated as a σ bond for H₂ and no bond for He₂. The absence of density between the nuclei is the distinguishing feature. It is of critical importance to realize that, at a sufficiently low contour level for the He₂ orbital, the plot would appear the same as the H₂ orbital. Thus, the contour choice is a critical factor in interpreting the chemical role of the orbital.

N₂ and F₂. A similar situation is encountered in the π orbitals of N₂ and F₂. The bonding π orbitals will look remarkably similar at a sufficiently low contour level, but this new technique permits them to be distinguished. Contour plots associated with the maxima in the ProDen functions for the π -bonding orbital in N₂ (40% ep) and the orbital of the same symmetry in F₂ (30% ep) along with plots of the ProDen functions are shown in Figure 3.

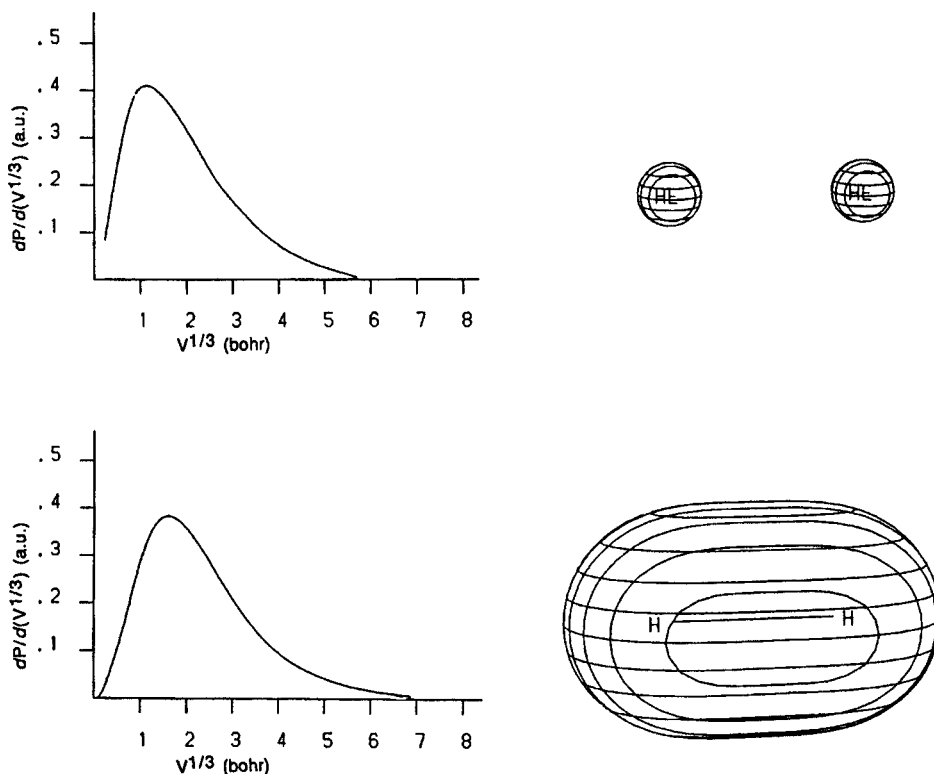


FIGURE 2. The probability density functions for the $1\Sigma_g^+$ orbital of H₂ and He₂ and orbital plots at the contour levels associated with the respective maxima.

Note that a large overlap between the nuclei is observed in the N_2 case, whereas the F_2 plot shows no concentration between the nuclei. The obvious interpretation is that the N_2 orbital represents a π bond, whereas the F_2 orbital does not. Thus, although both orbitals are allowed by symmetry to build up density between the nuclei, only the orbital that functions as a π bond (that of N_2) shows a concentration of density between the atoms.

It is important to note that the bond distance separating the two atoms in each of the preceding comparisons strongly influences the interpretation. If one shortens the bond length in either He_2 or F_2 to a bond length comparable to H_2 or N_2 , the selected contour plots depict bonding. Thus, although this technique provides a new method for the interpretation of molecular orbital calculations, trust in the results depends upon the confidence in the geometrical parameters. Obviously, any technique would be suspect if a calculation that is far from the equilibrium geometry yielded an interpretation consistent with the chemistry of the molecule at the equilibrium bond length. At the same time, small geometric changes (e.g., 0.05-Å variations in bond length) cause small effects on the interpretive

picture, but will obviously effect the quantitative evaluations.

HF. Figure 4 presents the ProDen function (on the left) for the $2A_1$ orbital of HF plotted in Figure 1. Note the presence of a peak at approximately 1.3 bohr. The associated contour level is 0.305 and contains 39% of the electron probability (39% ep). As seen in Figure 1, this contour level corresponds to a plot indicating significant H—F σ bonding. Note also the distinct shoulder that occurs in the probability density at approximately 1.0 bohr. The associated contour level is 0.370 and contains 28% of the electron probability (28% ep). The orbital plot at this contour level (Fig. 1) is interpreted as the fluorine lone pair. Thus, the presence of two local maxima in the ProDen function leads to the interpretation that this orbital is making significant contributions to both bonding and lone-pair character in the molecule.

It is worthwhile to compare the ProDen function with a simple plot of the amplitude (the contour level) versus the cubic root of the volume (on the right in Fig. 4). The amplitude squared yields the density. Note the smoothness of the curve. As the orbital plots make clear, something significant hap-

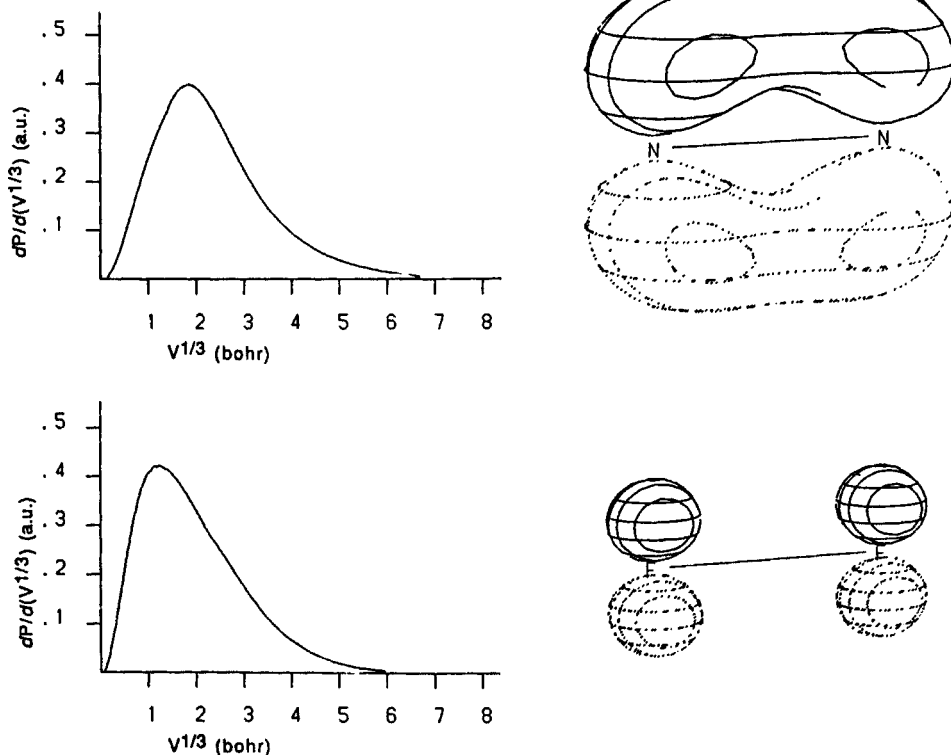


FIGURE 3. The probability density functions for one of the $1\Pi_g$ valence orbitals of N_2 and F_2 and orbital plots at the contour levels associated with the respective maxima.

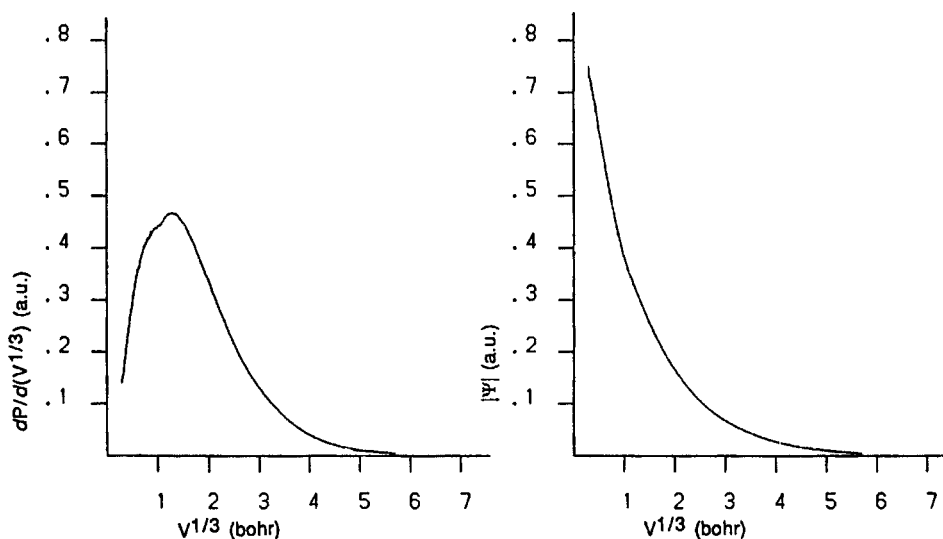


FIGURE 4. The probability density function for the $2A_1$ valence orbital of HF (left) and the contour level (right) plotted versus the cubic root of the volume for the same orbital. Orbital plots are in Figure 1.

pens as the amplitude is changed. It is this type of information, weighted by contributions from the volume, that is summarized in the ProDen function.

H_2O . The case of H_2O (Fig. 5) is small enough to allow convenient examination of all the valence orbitals simultaneously and still provides an example of slightly more complexity. The lowest energy valence orbital ($1A_1$) is understood to be a combination of an oxygen 2s orbital and the hydrogen 1s orbitals. The contour plot (44% ep) associated with the ProDen maximum depicts an orbital primarily composed of oxygen 2s that has been perturbed into the bonding region. The 2s orbital of the oxygen is hybridized (distorted by mixing with oxygen 2p) so that considerable density lies between the two hydrogen atoms and thus can be thought of as contributing equally to both O—H bonds. The next highest energy orbital ($1B_2$) is principally an oxygen 2p orbital that points at and mixes with the hydrogen s orbitals. It can clearly be identified from the associated orbital plot as a bonding orbital (39% ep). Note the presence of a modest shoulder near $V^{1/3} = 1$ bohr in the ProDen function. This area is associated with a contour that contains no hydrogen contribution and would depict a lone-pair contribution of unusual orientation. This orbital should contribute modestly, as judged by the contained probability, to lone-pair character as well as bonding character. The next orbital ($2A_1$) is the complement to the $1A_1$ orbital. It is a 2p orbital on oxygen hybridized with the 2s orbital to form what appears to be an oxygen lone pair because the orbital points away from the hydrogens—that is, there

is a significantly larger portion of the orbital on the side opposite to the hydrogens. There is constructive interference between the oxygen and hydrogen atoms, but no such density is observed in the plot associated with the maximum of the ProDen function (28% ep). This plot of the orbital would, thus, indicate lone-pair character. The presence of a small shoulder where $V^{1/3} = 2$ bohr is associated with bonding character, so this orbital does contribute to a lesser extent to bonding of the oxygen to the hydrogens. The HOMO ($1B_1$) is composed solely of oxygen 2p character as seen in the contour plot (33% ep) and is easily classified as a lone pair. The orbital plot does not change in basic shape as the contour level is varied and thus the ProDen calculation yields little new information. However, a comparison of the ProDen function with that of a free oxygen atom indicates that there has been some contraction in the molecular orbital.

The energy ordering of these orbitals makes sense chemically: the bond pairs are lower in energy than the lone pairs. The lone pair with significant 2s mixing is lower in energy than the lone pair that is predominantly 2p, yet still higher in energy than the bonding 2p orbital. Obviously, this simple interpretation does not present the complete picture. There is some component of O—H bonding in the $2A_1$ orbital, for instance, but the ProDen function provides a means to assess the different contributions. Whereas in the case of H_2O the simple model extracted from the calculation is well understood, the potential applicability for this method of analysis on more complicated systems is excellent.

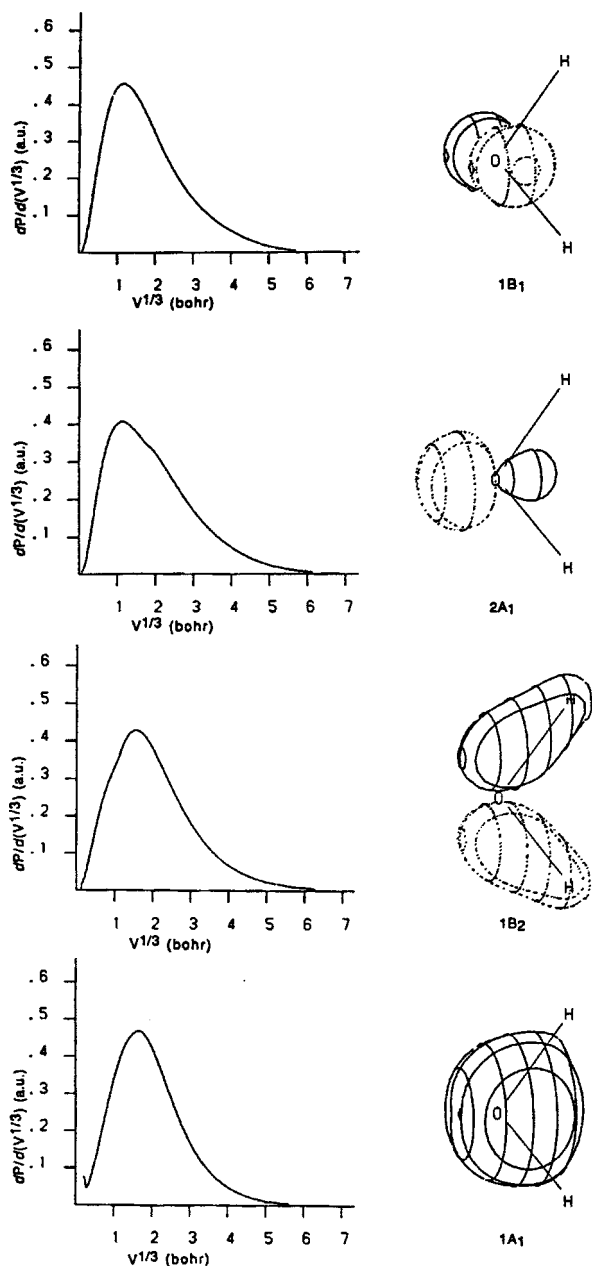


FIGURE 5. The probability density functions for the valence orbitals of H_2O and orbital plots at the contour levels associated with the respective maxima.

C_2H_6 . As noted earlier the ProDen function can indicate more than one feature to be significant by the presence of a shoulder or second peak. Such multiple distinctive features are commonly observed in hydrocarbon orbitals that involve C—C bonds. Ethane provides a good example. Although most of the orbitals have single, broad peaks that correspond exclusively to depictions of C—H bonding, the orbitals that contribute to the C—C bonds

also involve some measure of C—H bonding. The ProDen functions for the two A_{1g} orbitals are shown in Figure 6. Note that the 2A_{1g} curve has a second distinctive feature. In addition to the maximum at about 2 bohr (31% ep), there is a distinct shoulder at $V^{1/3} = 3$ bohr (about 60% ep). Arguably, this orbital has more than one chemical role.

The inner peak, the global maximum, occurs at a contour level that encloses density between the two carbon atoms and would be interpreted as the C—C bond. The outer shoulder is associated with a more delocalized picture; the associated contour level encloses density between all the atoms. However, a maximum in the ProDen function indicates a maximum in probability for the *volume immediately surrounding the depicted surface*. Because most of the depicted surface surrounds the C—H bonds, this contribution to the orbital would correspond to a C—H bond. The region of space associated with the C—C bond is far inside the depicted surface. Another useful technique in interpreting multiple maxima is to mentally subtract the volume of the smaller surface from the volume of the larger surface. This difference would more closely correspond to the electronic density represented by the larger surface. The outer maximum (lower contour) would correspond to the enclosed density without the C—C bonding depicted at the inner maximum (higher contour) and would thus correspond to C—H bonding.

The ProDen function for the ethane 1A_{1g} orbital has a maximum (52% ep) that corresponds to a highly delocalized C—H bond. This orbital contributes to all six C—H bonds simultaneously. However, at some higher threshold, the orbital plot would manifest C—C bonding character. A point was chosen from the peak in the 2A_{1g} orbital. Isosurface plots corresponding to the associated contour levels of both points are shown in Figure 6. Obviously, both orbitals contribute to both types of bonding—the C—C bonds and the C—H bonds, and this interpretative technique makes no attempt to break the symmetry of the system. The presence of peaks in the ProDen functions, however, makes it clear that the C—C bonding character is more important in the 2A_{1g} orbital, whereas the C—H bonding character is more important in the 1A_{1g} orbital.

$\text{Ni}(\text{CO})_4$. A final example comes from examining one of the HOMOs in $\text{Ni}(\text{CO})_4$. These T_{2g} orbitals are generally understood to be responsible for π backbonding in this complex. Figure 7 shows a plot of the ProDen function and two orbital plots at different contour levels. One plot corresponds to the

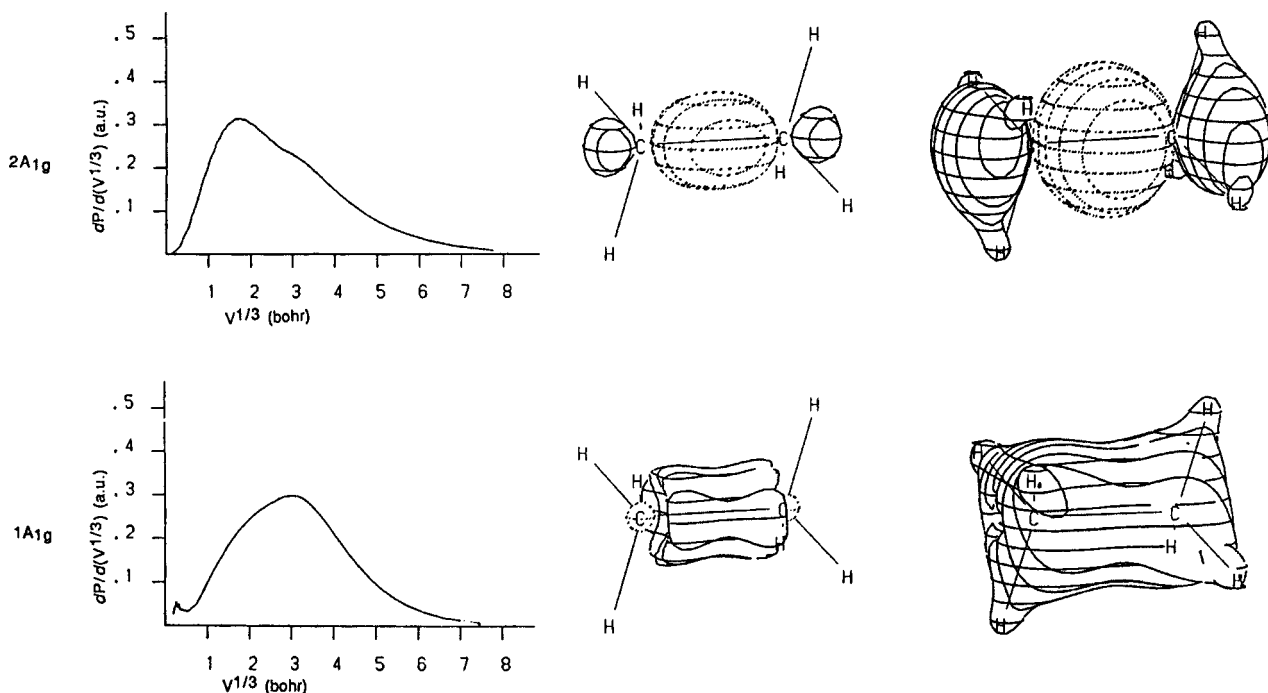


FIGURE 6. The probability density functions for the $1A_{1g}$ and $2A_{1g}$ valence orbitals of C_2H_6 and orbital plots at the contour levels associated with $V^{1/3} = 2$ bohr and $V^{1/3} = 3$ bohr for both orbitals. The contour level associated with the maximum of the $1A_{1g}$ orbital is at $V^{1/3} = 3$ and for $2A_{1g}$ is at $V^{1/3} = 2$.

global maximum, occurring around 1 bohr (20% ep). The other orbital plot corresponds to the distinct shoulder that is seen around 4.5 bohr (85% ep) in the ProDen function. The maximum corresponds to an orbital plot that is essentially a d orbital on the nickel atom. The outer shoulder, however, corresponds to that part of the orbital where the anti-bonding π orbital of the carbonyl ligand is occupied. This orbital is thus interpreted to be predominantly the d orbital on the metal, but with

substantial contributions to π backbonding. As this example illustrates, a choice of a single contour level can be unwise as the choice of either of the aforementioned options would miss an important aspect of the orbital's contribution. However, if forced to choose, because the inner contour level plot depicts a pure d orbital, a plot of the outer contour level would be preferred. It is worthwhile to note that very similar results were obtained for DFT calculations.

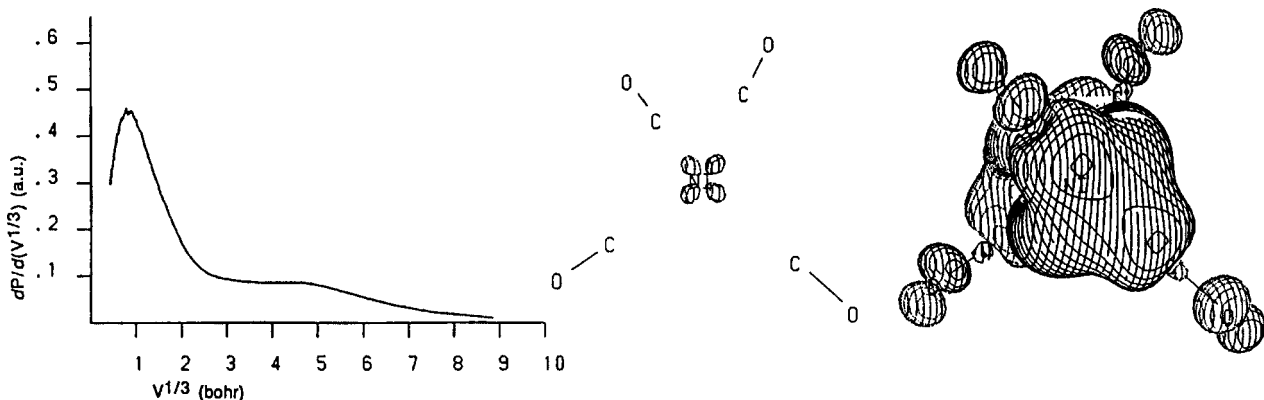


FIGURE 7. The probability density function for one of three degenerate T_{2g} orbitals that are the HOMOs of $Ni(CO)_4$, and orbital plots at the contour levels associated with the global maxima at $V^{1/3} = 1$ bohr and the secondary peak at $V^{1/3} \approx 5$ bohr.

Conclusion

This article proposes a technique for quantitatively assessing the relative importance of different isosurfaces for a three-dimensional density. A unique probability density function (ProDen) can be calculated for any molecular orbital. Every point of this function corresponds to a particular surface defined by a contour level or threshold, and the isosurface plot corresponding to the maximum of this new function depicts the region of highest probability. Therefore, the ProDen function provides a quantifiable basis for choosing one isosurface as a better representation than others and replaces the subjective conventions used heretofore. The isosurfaces associated with the maximum of this new function generally contain a small percentage 20% to 55% of the total probability and can often be interpreted in terms of a simple bonding description (bond pairs and lone pairs). Orbitals of identical symmetry and function (e.g., the bonding orbitals in H_2 and He_2 and those of N_2 and F_2) can be differentiated according to their chemical roles. In some orbitals the function shows multiple peaks (local maximum) and thereby indicates that the orbital contributes to more than one chemical role in the molecule. Examples of this are seen in orbitals from HF , H_2O , C_2H_6 , and $Ni(CO)_4$. The relative importance of these contributions may be assessed by peak heights in the ProDen function. This identification and quantification of different roles for a given molecular orbital goes beyond the qualitative picture presented by the orbital plots on their own, but this scheme does not separate such roles into different orbitals as many localization schemes do. In fact, the results of the ProDen calculations on molecular orbitals provide very different information from either localization schemes or atomic charges: this procedure allows for the quantitative association of chemical function with energy levels of the orbitals. Future work will apply this technique to chemical systems in which the bonding is less well understood and will expand the application of this technique beyond Hartree-Fock calculations.

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References

1. Refs. 2 to 10 are only a limited set of examples to demonstrate the point.
2. Wahl, A. C. *Science* 1966, 151, 961.
3. Dunning, T. W.; Winter, N. W. *J Chem Phys* 1971, 55, 3360.
4. Streitwieser, A.; Owens, P. H. *Orbital and Electron Density Diagrams*; Macmillan: New York, 1973.
5. Jorgensen, W. L.; Salem, L. *Organic Chemists Book of Orbitals*; Academic: New York, 1973.
6. van Wazer, J. R.; Absar, I. *Electron Densities in Molecules and Molecular Orbital*; Academic: New York, 1975.
7. Hoffmann, R. *Angew Chem Int Ed Engl* 1982, 21, 711.
8. (a) Hout, R. F.; Pietro, W. J.; Hehre, W. J. *J Comput Chem* 1983, 4, 276; (b) Hout, R. F.; Pietro, W. J.; Hehre, W. J. *A Pictorial Approach to Molecular Structure and Reactivity*; Wiley: New York, 1984.
9. Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chakravorty, S. J. *Acc Chem Res* 1993, 26, 628.
10. Knight, E. T.; Allen, L. C. *J Am Chem Soc* 1995, 117, 4401.
11. Two important techniques are found in: (a) Edmiston, C.; Ruedenberg, K. *Rev Mod Phys* 1963, 35, 457; (b) Edmiston, C.; Ruedenberg, K. *J Chem Phys* 1965, 43, 597; (c) Boys, S. F. In: Lowdin, P. O., ed. *Quantum Theory of Atoms, Molecules and the Solid State*; Academic: New York, 1966.
12. Prominent examples include: (a) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990; (b) Silvi, B.; Savin, A. *Nature* 1994, 371, 683.
13. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1978.
14. Albright, R. A.; Burdett, J. K.; Whangbo, M. *Orbital Interactions in Chemistry*; Wiley: New York, 1984.
15. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.
16. Fukui, K. *Acc Chem Res* 1971, 4, 57.
17. Coulson, C. A.; Longuet-Higgins, H. C. *Proc R Soc A* 1947, 192, 16.
18. Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988.
19. Mezey, P. G. In: Lipkowitz, K. B.; Boyd, D. B., eds. *Reviews in Computational Chemistry*, Vol. 1; VCH: New York, 1990.
20. Gerhold, G.; McMurchie, L.; Tye, T. *Am J Phys* 1972, 40, 988.
21. Most quantum chemistry textbooks have radial probability functions in them. See, for example: (a) Karplus, M.; Porter, R. N. *Atoms and Molecules*; Benjamin/Cummings: Reading, MA, 1970; (b) Matthews, P. S. C. *Quantum Chemistry of Atoms and Molecules*; Cambridge University Press: Cambridge, UK, 1986; (c) Dykstra, C. E. *Physical Chemistry: A Modern Introduction*; Prentice-Hall: Upper Saddle River, NJ, 1997.
22. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J Chem Phys* 1972, 56, 2257.
23. Wachters, A. J. H. *J Chem Phys* 1970, 52, 1033.
24. Rappe, A. K.; Smedley, T. A.; Goddard, W. A. *J Phys Chem* 1981, 85, 2607.
25. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J Am Chem Soc* 1980, 102, 939.

26. Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN-86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.
27. Jorgensen, W. L. QCPE Program No. 344, 1977. This program was modified to accept orbital coefficients and basis set information directly from the GAUSSIAN 86 checkpoint file.
28. A more reasonable number may be produced by finding the minimum between the two peaks and summing the probability associated with the two parts.